

The influence of structural Fe content in clay minerals on selenite redox kinetics

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Selenium (Se) is a rare element in the Earth's crust and is of significant concern due to the narrow gap between deficiency and toxicity to human health, as well as the long half-life of ⁷⁹Se in radioactive waste. The environmental fate of redox-sensitive Se is governed by its redox state. Important redox-active constituents of Earth's critical zone are Fe-bearing clay minerals, which also constitute the major components of the barrier in radioactive and other waste repositories. Although there are numerous reports on Se reduction by Fe-bearing clay minerals [1][2][3], the molecular redox mechanism still remains unsolved. This study systematically investigates selenite (Se(IV)O₃²⁻) sorption and reduction by Fe-bearing clay minerals of the smectite group, focusing on the influence of structural Fe(II) content in clay minerals. 2:1 dioctahedral smectite clay minerals with varying Fe content were reduced to obtain different Fe(II) contents. Kinetic batch experiments were conducted in a glovebox (O₂ < 0.1 ppm) for up to 720 or 3600 hours. X-ray absorption fine structure (XAFS) spectroscopy was used to identify the reduction products and their local structural environment in order to elucidate reaction mechanisms. Our results reveal a linear relationship between the content of structural Fe(II) and the rate of selenite reduction. Selenite is first adsorbed to clay edge sites by forming an inner-sphere sorption complex before being reduced to Se(0). The initial reduction product is amorphous, red Se(0), which gradually transforms into trigonal, grey Se(0). This transformation can be understood as the kinetically hindered conversion of an amorphous (or less crystalline) solid phase into the thermodynamically stable, more crystalline form of the solid. This insight into the selenite reduction mechanism provides valuable information for the development of effective approaches for selenite immobilization.

[1] Charlet L. et al. (2007), *Geochimica et Cosmochimica Acta* 71, 5731–5749. [2] Scheinost A. C. and Charlet L. (2008), *Environmental Science & Technology* 42, 1984–1989. [3] Scheinost A. C. et al. (2008), *Journal of Contaminant Hydrology* 102, 228–245.